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lowed by subsequent investigators in working out life histories of other forms, and there is no doubt now that the protozoan life cycle involves more or less definite asexual and sexual periods. In parasitic protozoa the sexual phase, including maturation, conjugation and fertilization, undoubtedly leads to renewed vigor of the race, or to a new power of asexual development, and to this extent at least, the time honored view of Bütschli's (1876) that conjugation is a means of the "Verjüngung" or rejuvenation of the cell, is warranted.

Associated with these alternate phases in the life history are the remarkable changes which accompany development of the sexual phase. These, involving the problems of sex, are particularly important in connection with the nuclear changes whereby a specific germinal chromatin is formed, sometimes at an early stage, in the asexual phase, and persisting as a germ plasm until used in the formation of gamete nuclei.

I have now given enough of the scope of protozoology to indicate that the protozoologist, far from being a strict specialist, rather immodestly claims the greater part of the whole field of biology as his own, and I would define protozoology, therefore, as that branch of the biological sciences which deals with the application of biological problems to, and with search for their solution in, the lowest group of animal organisms—the Protozoa.

GARY N. CALKINS

#### *SYNTHETIC METALS FROM NON-METALLIC ELEMENTS*<sup>1</sup>

It is one of the most striking facts of chemistry that three fourths of all the elements are metals. But it is no less re-

markable that metallic properties are confined exclusively to elements in the free state or, in case of alloys, to combinations of typically metallic elements.

In recent years the theory of the nature of the metallic state has been steadily developing into more and more precise form, so that to-day we have, in the electron theory of matter, a very satisfactory explanation for all of the characteristic properties of metals. Inasmuch as it is just a century since Davy proposed his celebrated metallic ammonium theory, we may now well consider whether metallic properties are, of necessity, confined to elements in the free state.

During the last two decades a vast amount of experimental evidence has been accumulating that electricity is granular in structure, though such a conclusion was strongly indicated three quarters of a century ago by Faraday's discovery of the facts epitomized in the law of electro-chemical equivalents as first pointed out by Helmholtz in 1881. The granules or ultimate atoms of electricity are now called corpuscles or electrons. The charge of the electron is negative in sign. In fact we have decisive experimental evidence of only this one kind of free electricity, positive electrification of a body, being from this standpoint merely a deficiency of electrons.

J. J. Thomson has shown how from the conception of an atom made up of electrons rotating in a sphere of positive electrification, there follows a simple explanation of many of the properties of an atom, including valence; a univalent atom, if negative, being one that can gain an electron, if positive, one that can lose an electron. A bivalent can gain or lose two electrons. A trivalent atom, three, etc. According to this hypothesis the most fundamental property of an atom of an element is this

<sup>1</sup> Read at the meeting of the American Chemical Society, Minneapolis, December, 1910.

tendency to gain or lose one or more electrons. The tendency to lose electrons is greatest for the alkali metals and least for the noble metals. According to this view, for example, sodium and chlorine react with great energy because of the great tendency for each atom of free sodium to lose an electron, on the one hand, and each atom of free chlorine to take up an electron, on the other. The action consists, therefore, in the transfer of an electron from an atom of sodium to an atom of chlorine. The components of a molecule of solid salt are therefore not an *atom* each of sodium and chlorine, but an *ion* of sodium combined with an *ion* of chlorine, if by the term *ion* we now mean atom  $\pm$  an electron.

The more or less complete "electrolytic dissociation" or "ionization" which occurs upon dissolving a salt in water is then due to the marked lessening of the electric force which holds together the ions of the solid salt by reason of the very great dielectric constant of water.

The application of the electron theory to the metallic state by Riecke, Drude, Lorentz, Thomson and others has led to results of the highest significance. Though the details of the relations of the electrons to the atoms are viewed somewhat differently by different physicists, it is however agreed by those who are working in this field that metals owe their most characteristic metallic properties of a physical nature to the *mobile* or free electrons which they contain. The absence of metallic properties in the solid non-metallic elements is, by this hypothesis, due to the supposed tendency of the atoms of such elements to *gain*, not lose, electrons: for which reason such a non-metallic solid will contain very few free or mobile electrons.

Thus, according to one view, electrons which are perhaps as numerous as the

atoms of the metal, move about freely among the atoms, with which they are considered to be in kinetic equilibrium. Electric conductivity is then due to the drift of these electrons under the influence of the potential in the wire. Thermo-conductivity of metals is explained equally satisfactorily by the electron hypothesis. The calculated ratio of thermal to electrical conductivity and also the temperature coefficient of the ratio are in good agreement with the facts. Other metallic properties, including opacity to light, reflecting and radiating power, the Hall effect, the Thomson effect, the Peltier effect, etc., are equally well accounted for.

The most characteristic chemical property of a metal is its ability to form the positive ions of salts. Every true metal has this property well developed. If we electrolyze a solution of a salt, say silver nitrate, the free positive ions of silver are attracted and move toward the negative electrode; on coming in contact with which each ion has forced into it an electron, which converts it into an atom of silver. The aggregate of such atoms deposited on the cathode has metallic properties; owing to the great tendency of each atom to give up an electron.

When we come next to consider the behavior upon electrolysis of a salt of a compound basic radical, it is difficult to see wherein its behavior should differ from that of a salt of a metallic element. In this case, as in the other, positive ions are attracted to the cathode, and upon striking the latter can gain electrons. If then the electron theory of the metallic state is as fundamental as it seems to be, the aggregate of such free "neutralized" radicals should be a body having metallic properties; in other words, a "synthetic metal." For such a hypothetical body would be made up of radicals, which, analogous to

metallic atoms, could easily lose electrons. The mass would then contain an abundance of mobile or free electrons and in such case possess high electrical and thermal conductivity, metallic luster, etc.

Turning now from theory to facts, the case of ammonium amalgam demands consideration at once on account of its historical importance. This remarkable substance was discovered practically simultaneously and independently by Seebeck, and by Berzelius in 1808; curiously enough, in just the same year that Davy isolated sodium and potassium from their hydroxides. Two years later Davy, in 1810, compared ammonium amalgam with the amalgams of sodium and potassium and was led to announce his famous ammonium hypothesis; the radical ammonium was analogous to the alkali metals and was said to exist in metallic form, united with the mercury, in ammonium amalgam. Berzelius and Ampere also supported this view. Some years later, after the discovery of other radicals, Dumas and Liebig in a joint paper gave Davy's idea a much more general form. They wrote: "Organic chemistry possesses its own elements which sometimes play the part of chlorine or oxygen, sometimes, however, also, that of a metal. Cyan, amid, benzoyl, the radicals of ammonia, the fats, the alcohols and their derivatives, form the true elements of organic nature." But the hypothesis of the metallic nature of ammonium in the amalgam did not pass unchallenged. Gay-Lussac and Thenard concluded that the so-called amalgam is only a mixture of ammonia, hydrogen and mercury; a view subsequently shared by many others, among them Seely, who found the volume of the inflated mass to be inversely proportional to the pressure upon it. The case against the metallic ammonium hypothesis was made still stronger by the evidence

furnished by an experiment by Landolt in 1868. If the amalgam is really analogous to sodium amalgam, if the radical actually has the properties of a metal, it should readily precipitate from solutions of their salts metals of smaller solution tension; but, in the test, Landolt could precipitate neither copper nor silver with ammonium amalgam.

The first really convincing evidence in favor of the ammonium hypothesis was furnished by LeBlanc in 1890. LeBlanc electrolyzed a solution of an ammonium salt with a mercury cathode. The apparatus was so arranged that simultaneous measurements of the polarization potential could also be made. This potential rose in a few minutes to a maximum which was nearly as great as that given by a sodium salt. The really important result, however, was observed after the polarizing current was cut off. The mercury cathode, which showed the inflation characteristic of ammonium amalgam, was still strongly electro-negative toward the solution and remained so for from ten to twenty minutes. That this effect was not due to hydrogen was shown by the fact that the hydrogen polarization potential was considerably smaller and that it fell off almost as soon as the current was interrupted. These experiments of LeBlanc, based as they were on the sound principles of electro-chemistry, gave a new impetus to the ammonium hypothesis. Coehn, in 1900, reasoned that if ammonium amalgam gave the high potential found by LeBlanc, it surely ought to precipitate copper and silver, and that Landolt's experiments should succeed. But Coehn failed exactly as did Landolt! Coehn next found that at very low temperatures, or even at zero, the amalgam was much more stable than at room temperature, and would precipitate copper from copper sulphate without difficulty.

This result was in itself insufficient to prove the metallic nature of ammonium, since free hydrogen was always present in the amalgam, and may have been the active substance in the reaction. To remove any doubt, Coehn then showed that not only are cadmium and zinc precipitated by the cold amalgam, but that barium amalgam results from the action at zero of ammonium amalgam on a solution of barium chloride. This fact was independently discovered later by G. M. Smith, who also obtained sodium and potassium amalgams in a similar manner. Thus the experiments of LeBlanc, Coehn and G. M. Smith furnish indisputable evidence of the metallic nature of ammonium in ammonium amalgam.

It is often stated that metals are insoluble in a physical sense, in all solvents excepting other metals. This statement can scarcely be upheld in view of the recent work of Kraus, on solutions of sodium, potassium, calcium, etc., in liquid ammonia. These very unique solutions, discovered by Weyl in 1864, seem to have many distinctive metallic properties. They are practically opaque, except when very dilute; even in this respect they resemble gold, which is transparent in very thin layers. They also show metallic luster, and reflection, and while they conduct the electric current, the conduction seems to be metallic rather than electrolytic in character. Upon evaporation, they deposit the pure metal in crystalline form. All such solutions, if sufficiently dilute, have a characteristic deep blue color. Now Palmaer has shown that by the electrolysis of tetraalkyl ammonium salts dissolved in liquid ammonia, unstable blue solutions are formed about the cathode. These blue solutions were thought to contain the organic radical in metallic form dissolved in ammonia. These facts have

been confirmed by Kraus, who also concurs in the explanation. .

LeBlanc's experiments on the polarization of mercury in solutions of ammonium salts, were also extended to include a similar study of salts of a number of substituted ammonias. Mono-, di- and tetramethyl and mono-ethyl ammonium ions gave results more or less like those of ammonium ions, from which facts LeBlanc concluded that in these cases also amalgams were formed, although none of the supposed amalgams were isolated. When attempts were made by Dr. Moore and myself to obtain an amalgam by the electrolysis of aqueous solutions of tetramethyl ammonium salts the results were complete failures; not a trace of amalgam could be isolated. But when we substituted absolute ethyl alcohol for water, as solvent, the amalgam resulted at once.<sup>2</sup> This amalgam differs greatly from ammonium amalgam in both appearance and stability. It is a crystalline solid of metallic luster, closely resembling sodium amalgam. It can be kept for days at temperatures below +10 degrees and does not have any tendency to become inflated. Its density is somewhat less than that of mercury, but still many times greater than that of ammonium amalgam. Its electrical conductivity is comparable to that of a metal. Chemically, it resembles the alkali metal amalgams, but is far more active than that of sodium. It reacts with water with great energy and rapidity, giving hydrogen and the corresponding base, tetramethyl ammonium hydroxide. From solutions of salts of copper and zinc, these metals are precipitated at once; while from solutions of salts of sodium and potassium the corresponding amalgams are formed. With solutions of ammonium salts the charac-

<sup>2</sup> McCoy and Moore, *SCIENCE*, **30**, 315 (1909); *J. Amer. Chem. Soc.*, **33**, 273 (1911).

teristic inflated mass of ammonium amalgam is produced.

The very high electrolytic solution tension indicated by these reactions is confirmed by direct potential measurements. The values obtained, for similar conditions, are about .6 volt higher than those found recently by Lewis and Kraus for sodium amalgam. This result is in harmony with the enormously greater activity towards water of the organic amalgam. Dr. Moore and I have also made mono-methyl ammonium amalgam and studied its properties.

The facts just discussed point clearly to the probability that in general positive ions, if free, or even amalgamated with mercury, will possess metallic properties. Practically, however, several causes may prevent the isolation of such metallic bodies. We know that it is not possible by electrolysis to separate many metals like sodium from aqueous solutions of their salts. Similar relations may obtain in the electrolysis of an organic salt. On the other hand, it is theoretically possible that such a compound metal may be so unstable in the free state that it suffers spontaneous decomposition at the moment of its formation from its ions. A third possibility is exemplified by the case of hydrogen. For a long time it was thought by some chemists that hydrogen in solid form would have metallic properties, since acids may be considered "hydrogen salts." The fact that solid hydrogen is now known to have no metallic properties proves clearly the fallacy of the old idea and seems to be also a flat contradiction of the hypothesis in question.

Now, hydrogen differs from the metals in one other important respect: while the molecules of metallic vapors are always monatomic those of hydrogen are diatomic. Thomson has considered the question of

the theory of the union of two like atoms to form a molecule of an elementary gas, and has shown very convincingly that it is reasonable to conclude that one atom sends its valence electron into the other and that the combination is entirely analogous to that when two unlike atoms combine. If this is the case, it is possible to understand why solid hydrogen has no metallic properties; its valence electrons are *bound* and not *free* nor *mobile*. Analogously to hydrogen, some organic radicals which can form positive ions of salts may unite in pairs to form double radicals. These would not be expected to have metallic properties.

In some cases, however, even hydrogen seems to have some metallic properties; it dissolves readily in palladium and, when nascent, diffuses easily through iron. The latter property of hydrogen may be due to continued existence in the monatomic and therefore metallic state.

As I have tried to point out, the electron theory of the metallic state would lead us to expect that free radicals, formed by the neutralization of the positive ions of salts by the introduction into each ion of that number of electrons represented by its valence would have metallic properties. The facts just reviewed, though few in number, seem to me to lend support to this hypothesis, and to lead to the conclusion that it is possible to prepare composite metallic substances, which may be termed synthetic metals, from constituent elements, some of which at least are non-metallic.

HERBERT N. MCCOY

December 28, 1910

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WILLIAM RUSSELL DUDLEY.

WILLIAM RUSSELL DUDLEY, professor of systematic botany in Stanford University, was born on a farm in North Guilford, Conn.,